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Technical Report S-242

SYNTHESIS OF HTPB AND CTPB PREPOLYMERS BY
ANIONIC AND FREE-RADICAL POLYMERIZATION (U)

by

Samuel F. Reed, Jr.

January 1970

U. S. ARMY MISSILE COMMAND
REDSTONE ARSENAL, ALABAMA 35809

Contract DAAH01-69-C-0772

ROHM AND HAAS COMPANY
REDSTONE RESEARCH LABORATORIES
HUNTSVILLE, ALABAMA 35807

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FOREWORD

The work described in this report was performed under Contract DAAH01-69-C-0772 for exploratory development of propellants for missiles and rockets under the technical cognizance of the Solid Propellant Chemistry Branch, Army Propulsion Laboratory and Center, Research and Engineering Directorate, U. S. Army Missile Command.

This report discusses the synthesis and characterization of hydroxyl- and carboxyl-terminated polybutadiene polymers. These polymers are of interest as binders for solid propellants having wide temperature limits. Preliminary studies on the anionic polymerization of butadiene were reported in Technical Report S-185 and studies on the free radical polymerization of dienes were reported in Technical Report S-196.

Special acknowledgement is made to Mr. R. D. Strahm and Dr. K. E. Johnson of these Laboratories for their contributions to this program. The technical assistance of Mrs. Alice Glover and Mr. J. O. Woods is appreciated.

ABSTRACT

This report describes the synthesis and characterization of polybutadienes and polyisoprenes possessing hydroxyl and/or carboxyl functionality. Polymer formation was accomplished through anionic or free radical initiated reactions. Characterization of the materials involved analyses for molecular weight, molecular weight distribution, microstructure, end-group content, and solution viscosity. The objectives of the program were to scale up the anionic polymerization of butadiene to produce a superior HTPB prepolymer, and to prepare by free radical techniques superior HTPB as well as hydroxyl- and carboxyl-terminated isoprene polymers for solid propellant binders.

Large-scale (100 gm) anionic polymerization of butadiene was carried out with two different dilithio initiators. A prepolymer (HTPB) exhibiting greater uniformity in properties was obtained with a commercial initiator than with an initiator prepared in-house. Functionality of the HTPB prepolymer ranged from 1.7 to 0.1 with average values near 1.0. In most respects these materials were comparable to similar commercial prepolymers. Preliminary gum stock and propellant development studies with the prepolymer confirmed their suitability as propellant binders.

Free radical polymerizations of butadiene and isoprene were carried out to give sufficient quantities of prepolymers for propellant development studies. Emphasis was focused on the preparation of HTPI and CTPI because the cis-1,4 form of polymer should lead to favorable low-temperature properties of these materials. Polymerizations carried out in various solvents demonstrated that the solvent has little effect on properties of the prepolymer. An important discovery was that the polymerization temperature plays an important part in determining the molecular weight distribution of the prepolymers formed in free radical polymerizations. Reactions leading to HTPB or HTPI conducted at 60°C or lower exhibited a polydispersity of 1.3 or less.

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Section I. (U) INTRODUCTION

(U) Several polybutadienes, either hydroxyl-terminated (HTPB) or carboxyl-terminated (CTPB) are available for use as solid propellant binders. These include Thiokol's HC-434, Sinclair's Poly B-D[®] R-45M, and anionic polymers such as Phillip's Butarez[®] materials. For the reasons outlined below, none of the polydienes commercially available offers the ultimate in mechanical properties, particularly at low temperatures. This has prompted a program in the synthesis of functionally-terminated polydiene polymers for use as binders in solid propellant systems.

(U) Our preliminary studies of the anionic polymerization of butadiene established that an HTPB polymer with properties superior to those of Butarez HT could be prepared in small quantities. This experimental polymer had a high functionality (near 2.0), the desirable microstructure (up to 80% 1,4 polymerization), and a good molecular weight distribution (\bar{M}_w/\bar{M}_n were low); however some difficulty was encountered in preparing polymers of reproducible molecular weights.

(U) Section III of this report deals with the anionic polymerization of butadiene on a larger scale (100-gm runs) to see whether an HTPB polymer with superior properties could be produced in quantities sufficient for propellant development studies.

(U) Section IV of the report describes the results of free radical polymerization studies leading to the preparation of functionally-terminated polybutadienes and polyisoprenes. An improvement in low-temperature mechanical properties of solid propellants formulated with these binders, particularly the polyisoprenes, might be expected for the reasons that follow.

(U) The usual preparative techniques for polydienes give polymers composed of different structural forms, depending upon whether the diene monomer is incorporated into the chain in a 1,4-addition (cis-trans forms), 1,2- or 3,4-addition (vinyl forms), or a combination of these additions. Structural forms of the polydiene are commonly referred to as the microstructure of the polymer. The relative proportion of each microstructural form in the polydiene is dependent upon the specific conditions of the polymerization and upon the specific diene monomer. The low temperature properties of the polydiene are

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highly dependent upon the microstructure of the polymer; the microstructure determines the glass transition temperature (T_g) of the polymer, and T_g defines the modulus and tensile properties of the polymer.

(U) A brief comparison of available polydiene binder materials has been attempted, using the glass transition temperature (T_g) to define the character of the polymer's low temperature properties. The T_g is a useful property for comparative purposes since it defines the lower temperature limits at which the polymer will be useful as an elastomeric material. T_g's of polymeric materials have also been shown to be related to other polymer properties: hardness, brittleness, flexibility, toughness, and tackiness. Assuming the polydiene to be a copolymer or terpolymer of differing microstructural forms (cis-1,4, trans-1,4, and vinyl), and the T_g of the polymer to reflect the concentration of each form, one may calculate the T_g of the polydiene using the equation:

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} + \dots + \frac{W_N}{T_{gN}} \quad \underline{1}$$

in which W is the weight fraction of monomer A, B....N in the polymer and T_{gA}, T_{gB}, etc. are the T_g values of the homopolymers. T_g values are expressed in degrees Kelvin.

(U) Applying the T_g calculations to polydienes which are currently being used, to some prepared in this study, and to some hypothetical examples gave the results reported in Table I. HC-434 and R-45M are representative of a CTPB and a HTPB, respectively, prepared by a free-radical mechanism. Their calculated T_g values are -37° and -35°C, and are slightly higher than the value calculated (-44°C) for the Butarez HT polymer prepared by anionic initiation. This difference in T_g between the free radical and anionic formed polybutadienes is attributed to the higher cis-1,4 content of the latter.

(U) The major conclusion arising as a result of the T_g calculations is that functional group-containing polyisoprenes and polychloroprenes may offer certain advantages in low temperature properties over similar polybutadienes. It is true that an all cis-1,4-polybutadiene would exhibit superior low temperature properties, but a high cis-1,4 content is not likely to be realized through any known practical preparation technique for HTPB and CTPB polymers.

Table I. (U) Tg of Some HT- and CT-Polydienes

| No. | Polydiene | Microstructural Form, Weight % | | | Tg | |
|-----|-----------------------------|-----------------------------------|----------------------|----------------------|-------|-------|
| | | Cis _{1,4} | Trans _{1,4} | Vinyl _{1,2} | °K | °C |
| 1 | HC-434 ^a | 18.2 | 57.2 | 24.6 | 235.1 | -37.1 |
| 2 | R-45M ^b | 15.96 | 61.2 | 22.8 | 238.1 | -34.9 |
| 3 | Butarez HT ^c | 25.2 | 43.6 | 31.1 | 228.8 | -44.2 |
| 4 | IH-CTPB ^{a,d} | 17.4 | 59.5 | 22.8 | 237.0 | -36.0 |
| 5 | IH-HTPB ^c | 31.5 | 48.1 | 20.5 | 220.3 | -52.7 |
| 6 | IH-CTPI ^{a,e} | 78.6 | - | 23.4 | 212.3 | -55.7 |
| 7 | Polybutadiene ^f | 20.0 | 50.0 | 30.0 | 233.6 | -39.4 |
| 8 | Polybutadiene ^f | 30.0 | 50.0 | 20.0 | 221.7 | -51.3 |
| 9 | Polybutadiene ^f | 75.0 | 0 | 25.0 | 218.3 | -54.7 |
| 10 | Polyisoprene ^{f,h} | 85.0 | 0 | 15.0 ^g | 210.5 | -62.5 |

^a Polymers formed by free radical initiation, carboxyl-terminated.

^b Polymers formed by free radical initiation, hydroxyl-terminated.

^c Polymers formed by anionic initiation, hydroxyl-terminated.

^d An average microstructure content of CTPB formed in four reactions.

^e An average microstructure content of CTPI formed in four reactions.

IH-CTPB

In-house CTPB

IH-HTPB

In-house HTPB

IH-CTPI

In-house HT-polyisoprene

^f Hypothetical cases.

^g Polyisoprenes prepared by free radical polymerizations contain 75-80% of the isoprene in the cis-1,4 configuration.

^h The vinyl-1,2 and -3,4 configurations were combined and assumed to possess a Tg of 300°K.

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(U) Section IV of this report, then, deals with the synthesis, by free radical initiation, of diene polymers containing a high percentage of cis-1,4 microstructure.

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Section II. (C) SUMMARY AND CONCLUSIONS (U)

1. (U) Anionic Polymerizations

(U) A total of 28 anionic polymerizations of butadienes was carried out; the polymers were hydroxyl-terminated via ethylene oxide. Both a dilithiopolyisoprene initiator, prepared in batches for each polymerization, and a commercial initiator, Lithium Corporation of America's DiLi-1, were used.

(U) The polymers prepared from the batch-type initiator varied considerably in their properties. Molecular weights (\bar{M}_n) ranged from about 14,000 to 3,700, intrinsic viscosities ranged from 0.12 to 1.4, polydispersity ranged from 1.3 to 2.6, and functionality varied from 0.11 to 1.72. Considerable variation in the microstructure of the polymers was noted.

(U) The polymers prepared from the DiLi-1 initiator had a higher degree of reproducibility. Molecular weights (\bar{M}_n) ranged from 4,100 to 7,800, the intrinsic viscosity range was 0.08 to 0.35, polydispersity varied from 1.13 to 1.62, and functionality, although poor, ranged from 0.14 to 1.61.

(U) In most of their properties, the anionic polymers were about equal to commercial polymers such as Butarez HT; they certainly were not superior to any commercial materials. Thus, the difficult experimental techniques of this polymerization method are of questionable utility on a large scale. No further scale-up studies are planned.

2. (C) Free Radical Polymerizations (U)

(U) The free radical polymerization of butadiene and isoprene was examined; 4,4'-azobis(4-cyanovaleric acid) (AMCV) and 2,2'-azobis(5-hydroxy-2-methylvaleronitrile) (AMHV) were used as initiators. Polymerization reactions were carried out on 100-gm scale with butadiene and isoprene; HTPB, CTPB, HTPI, and CTPI polymers were produced and characterized.

(U) A series of 9 polymerizations of butadiene with 3 mole % AMHV gave polymers relatively uniform in character. The yields of polymer ranged from 54 to 76%, the molecular weight values ranged from 2,600 to 4,300, and functionality values varied

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from 2.16 to 3.18. The microstructure of the polymers changed little; the ratio of cis-1,4:trans-1,4:vinyl was about 16:61:23. When the initiator concentration was increased to 10 mole %, the molecular weight decreased to about 2,000.

(U) The properties of the CTPB polymers were similar to those of the HTPB polymers, except the molecular weights ranged from 3,100 to 8,500.

(C) Special attention was given to the HTPI and CTPI polymers. Their microstructure (75-80% cis-1,4) establishes these materials as promising candidates for solid propellant binders. The molecular weights (\bar{M}_n) of the HTPI polymers ranged from 2,300 to 3,300; functionality values of 1.35 to 2.53 were noted. The CTPI polymers had higher molecular weights (2,300 to 4,800) and higher functionality (1.61 to 3.30).

(U) Solvent effects on prepolymer properties appeared to be of little concern in the free radical initiated reactions. No significant change in property values could be detected when butadiene was polymerized in dioxane, acetonitrile, or dimethylformamide other than the expected higher molecular weight of products prepared in dioxane.

(U) A series of polymerizations carried out at varying temperatures produced a most unexpected result. It was found that butadiene or isoprene polymerizations carried out at 60°C or lower gave prepolymers with unusually low molecular weight distributions (< 1.3). In contrast, prepolymers prepared at 70°C or above displayed molecular weight distributions (> 1.4). This result represents the most significant discovery of the synthesis program because it eliminated one of the most serious drawbacks towards the application of free radically formed prepolymers as propellant binders. Heretofore, no prepolymers of this type possessing low polydispersities had been available for study. It would appear that free radically formed prepolymers are now competitive with those prepared by anionic initiation in terms of molecular weight distribution.

(U) Further studies are continuing in this program on temperature effects influencing polydiene properties. A complete evaluation of this discovery is important to the ultimate development of polydiene binder materials and to advance the current state of the art in this field.

Section III. (C) ANIONIC POLYMERIZATION (U)

1. (U) General Comments

(U) Basically, there are two general techniques for conducting an anionic polymerization in order to protect the reaction from oxygen and moisture. The first involves the use of an inert atmosphere (nitrogen, helium, argon) throughout the polymerization reactor; the second involves the use of an evacuated system. It was found that more consistent reproducibility in polymer properties was obtained when the polymerizations were conducted in an evacuated system. Consequently, the results described in this report were obtained from vacuum-line experiments. A rather detailed description of vacuum-line techniques suitable for anionic polymerizations has been reported by Fetters (1)¹.

(U) There are usually several steps involved in the anionic polymerization method. Those are: (a) equipment and reagent preparation, (b) initiator preparation, (c) diene polymerization, (d) termination, (e) hydrolysis of the lithium salt, and (f) polymer isolation. A detailed description of each step in the polymerization process and the methods for characterizing the prepolymers have been given in a previous report (2).

2. (U) Results and Discussion

a. (U) Polymerization

(U) The major objective of this program was to investigate the anionic polymerization of butadiene and the preparation of HTPB binder materials on a scale sufficient to supply the prepolymer for propellant evaluation studies. The reactions were carried out on a 100-gram scale. Specific objectives were to determine the reproducibility of the prepolymer properties and the suitability of the prepolymer as a propellant binder material.

¹ Numbers in parentheses refer to references at the end of the report.

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(U) Following the general procedure discussed earlier in this report, a total of 28 polymerization reactions were performed, the products isolated, and characterized. In the first series of 15 reactions, each reaction was initiated with a dilithiopolyisoprene solution prepared (1) individually for the specific reaction. The initiator used in the second series of 13 reactions was a commercial material (DiLi-1) purchased from the Lithium Corporation of America.

(U) DiLi-1 is a dilithium-isoprene oligomer mixture in a benzene-dimethyl ether solution (4). The weight percent composition of the solution is 11% oligomers, 6-7% dimethyl ether, and 82% benzene. The oligomer mixture consists of 75 to 90 mole % dilithium-diisoprene, 7 to 22 mole % dilithium-triisoprene, and 2 to 3 mole % dilithium-tetraisoprene. The solution is approximately 1.15N in active base and contains 5 mole % or less of a monofunctional dimer fraction. In many ways this initiator solution is similar to that prepared in-house (2).

(1) (U) Series I Prepolymers - Use of Dilithiopolyisoprene Initiator

(U) The experimental data for the first series of 15 reactions using the initiator prepared in-house are shown in Table II. In all instances, the polymerization was terminated by reacting the active polymer with ethylene oxide over a period of several days. At the point of introducing the ethylene oxide, a gel was obtained in all but one reaction, i. e., 97B. Methods of hydrolysis and prepolymer isolation have been described previously (2). The yields reported in Table II represent the yields of the purified products. Usually, 2 to 5% of the polymer was retained in the solvents (ether-methanol) used in the purification process.

(U) Characterization data obtained on the HTPB prepolymers are displayed in Table III. Table III contains molecular weight, end group, viscosity, microstructure, and gel permeation data. These data are indicative that the prepolymers vary considerably in their properties although prepared under very similar conditions. For instance, molecular weights (\bar{M}_n) ranged from approximately 14,000 to 3,700, intrinsic viscosities from 1.4 to 0.12, and polydispersity from 2.6 to 1.3. The lack of reproducibility in polymer properties may be attributed to the inability quantitatively to effect

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transfer of the initiator solution from the initiator preparatory flask to the polymerization flask (2). In addition, the reprecipitation procedure (purification) produces random variations in the samples and, hence, leads to less reproducibility in certain properties.

Table II. (U) HTPB Prepolymers. Experimental Data for Series I

| No. | Initiator Preparation | | | | Solvent (ml) | Solvent Removed (ml) | [B] (ml) | Time (hr) | Gel | Yield (%) |
|----------------------|-----------------------|------|------|----------------------|------------------------|----------------------|----------|-----------|-----|-----------|
| | [S] ^a | [Li] | [I] | [Ether] ^b | | | | | | |
| 90B | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 825 | 155 | 21 | Yes | 91.7 |
| 93B | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 800 | 158 | 19 | Yes | 77.2 |
| 94B ^c | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 800 | 82 | 19 | Yes | 83.7 |
| 95B | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 805 | 158 | 19 | Yes | 86.1 |
| 96B | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 800 | 148 | 16 | Yes | 86.9 |
| 97B ^{d, f} | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 810 | 150 | 20 | No | 67.6 |
| 98B ^f | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 800 | 150 | 22 | Yes | 94.2 |
| 99B ^f | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 800 | 150 | 16 | Yes | 96.4 |
| 100B | 1.5 | 1.5 | 21.0 | 400 | DEE ^b -1200 | - | 150 | 18 | Yes | 93.3 |
| 101B ^f | 1.5 | 1.5 | 21.0 | 400 | Tol-2000 | 850 | 160 | 18 | Yes | 92.8 |
| 102B ^{e, f} | 2.25 | 1.5 | 21.0 | 400 | Tol-2000 | 800 | 165 | 17 | Yes | 86.2 |
| 103B ^f | 2.25 | 1.5 | 21.0 | 400 | Tol-2000 | 600 | 140 | 18 | Yes | 92.1 |
| 104B ^f | 2.25 | 1.5 | 21.0 | 400 | Tol-2000 | 775 | 155 | 16 | Yes | 94.0 |
| 105B ^f | 2.25 | 1.5 | 21.0 | 400 | Tol-2000 | 800 | 145 | 18 | Yes | 82.2 |
| 106B ^f | 3.0 | 1.5 | 21.0 | 400 | Tol-2000 | 900 | 150 | 23 | Yes | 93.3 |

- ^a S = Stilbene
^b Diethyl Ether
^c Approximately 1/2 scale reaction
^d New ethylene oxide cylinder used
^e Vacuum system leaked overnight
^f Extra purification of solvent

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| Table III. (U) Characterization Data for HTPB Prepolymers - Series I | | | | | | | | | | | |
|--|-------------|-------------|----------------------|------------------|-------------------|-----------|-------|---------------|-------------|------|------------|
| No. | \bar{M}_n | Weight % OH | Equivalent Weight OH | Functionality OH | Microstructure, % | | | G. P. C. Data | | | [η] |
| | | | | | Cis-1,4 | Trans-1,4 | Vinyl | \bar{A}_w | \bar{A}_n | PD | |
| 90B | 12800 | 0.18 | 9450 | 1.35 | 19.46 | 38.91 | 26.38 | | | | |
| 93B | 10000 | 0.11 | 15450 | 0.65 | 19.11 | 43.37 | 37.89 | 1191 | 919 | 1.30 | 0.860 |
| 94B | 8100 | 0.22 | 7700 | 1.05 | 18.12 | 42.07 | 37.38 | 669 | 414 | 1.62 | 0.410 |
| 95B | 7700 | 0.08 | 21500 | 0.36 | 17.72 | 35.50 | 40.69 | 1099 | 632 | 1.74 | 0.545 |
| 96B | 5600 | 0.47 | 3625 | 1.54 | 21.09 | 43.50 | 30.16 | 446 | 304 | 1.46 | 0.293 |
| 97B | 14000 | 0.05 | 34000 | 0.50 | 17.17 | 35.43 | 40.84 | 1880 | 731 | 2.57 | 1.400 |
| 98B | 5400 | 0.37 | 4600 | 1.17 | 19.01 | 38.87 | 34.42 | 636 | 369 | 1.73 | 0.278 |
| 99B | 5900 | 0.45 | 3775 | 1.56 | 20.20 | 40.88 | 28.22 | 406 | 258 | 1.58 | 0.275 |
| 100B | 4000 | 0.63 | 2700 | 1.48 | 17.75 | 65.07 | 9.14 | 269 | 198 | 1.36 | 0.170 |
| 101B | 10300 | 0.20 | 8500 | 1.21 | 20.68 | 44.30 | 30.17 | 755 | 460 | 1.64 | 0.420 |
| 102B | 8200 | 0.36 | 4775 | 1.72 | 16.86 | 38.64 | 39.32 | 1046 | 414 | 2.52 | 0.325 |
| 103B | 8500 | 0.24 | 7150 | 1.19 | 16.90 | 36.05 | 36.55 | 688 | 402 | 1.71 | 0.283 |
| 104B | 5500 | 0.45 | 3715 | 1.46 | 18.47 | 40.24 | 33.07 | 489 | 309 | 1.59 | 0.190 |
| 105B | 1400 | 0.13 | 13100 | 0.11 | 17.81 | 37.41 | 40.96 | 928 | 503 | 1.84 | 0.500 |
| 106B | 3700 | 0.71 | 2400 | 1.54 | 20.58 | 43.69 | 28.84 | 233 | 175 | 1.33 | 0.120 |

(U) A relatively high degree of variation was observed in the microstructure of the prepolymers, particularly in the trans-1,4 and vinyl contents. The weight and number average Angstrom lengths of the polymers varied over a rather wide range, also. Functionality of the prepolymers ranged from 1.72 to 0.11 with a value of 1.13 being average. Several of the values were exceptionally low, and likely reflect errors associated with measurements of \bar{M}_n and end-group analysis rather than actual low functionality values. It is believed that the functionality of the prepolymers, in these instances, is higher than demonstrated by the analytical data. This is verified to some extent by the successful use of these prepolymers in propellant compositions, as reported later in this report.

(2) (U) Series II Prepolymers - Use of DiLi-1 Initiator

(U) The experimental data for the butadiene polymerizations employing the DiLi-1 initiator are shown in Table IV. Using DiLi-1 eliminated the initiator preparation step and simplified the entire procedure. A constant volume of the DiLi-1 solution (50 ml) was used in all reactions with solution transfer made by syringe. Gel formation was observed in only 5 reactions, although

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other reaction mixtures did give an observable increase in viscosity on addition of the ethylene oxide. Yields (87-99%) were very good and, generally, slightly higher than obtained in Series I reactions.

| Table IV. (U) HTPB Prepolymers. Experimental Data for Series II | | | | | | |
|---|----------------|-----------------|---------------|--------------|-----|-------|
| No. | DiLi-1 (ml) | Solvent (ml) | [B] (ml) | Time (hr) | Gel | Yield |
| 108B | 50 | Tol-2000 | 150 | 20 | Yes | 98.4 |
| 109B | 50 | Tol-2000 | 150 | 20 | Yes | 99.0 |
| 111B | 50 | Tol-2000 | 150 | 19 | Yes | 99.0 |
| 114B | 50 | Tol-2000 | 155 | 18 | Yes | 97.3 |
| 115B | 50 | Tol-1600 | 150 | 21 | No | 94.3 |
| 116B | 50 | Tol-1600 | 148 | 21 | No | 90.3 |
| 117B | 50 | Tol-1600 | 140 | 21 | No | 88.5 |
| 118B | 50 | Tol-1600 | 150 | 20 | No | 92.2 |
| 120B | 50 | Tol-1600 | 150 | 6 | No | 93.3 |
| 121B | 50 | Tol-1600 | 150 | 20 | Yes | 93.3 |
| 122B | 50 | Tol-1600 | 155 | 20 | No | 89.9 |
| 124B | 50 | Tol-1600 | 150 | 18 | No | 92.2 |
| 126B | 50 | Tol-1600 | 155 | 21 | No | 87.4 |

(U) Characterization data are shown in Table V. In general, there was a higher degree of reproducibility in property values of the polymers than observed in Series I polymers. For instance, the molecular weight (M_n) range was 4100 to 7800, the intrinsic viscosity range was 0.08 to 0.35, and polydispersity varied from 1.13 to 1.62. Other properties, including microstructure and G. P. C. data, were more uniform in character.

(U) Again there was a notable difference in the end-group analyses. The weight percent hydroxyl group content of the prepolymers ranged from a high of 0.49 to a low of 0.06. Consequently, these results affected the calculated equivalent weights and functionality values, both displaying a wide range of values. The average functionality was found to be 0.88.

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| Table V. (U) Characterization Data for ITPB Prepolymers -Series II | | | | | | | | | | | |
|--|-------------|----------------|---------------------------|---------------------|-------------------|-----------|-------|---------------|-------------|------|------------|
| No. | \bar{M}_n | Weight % OH | Equivalent Weight % | Functionality OH | Microstructure, % | | | G. P. C. Data | | | [η] |
| | | | | | Cis-1,4 | Trans-1,4 | Vinyl | \bar{A}_w | \bar{A}_n | PD | |
| 108B | 5600 | 0.49 | 3470 | 1.61 | 20.87 | 34.95 | 44.01 | 374 | 261 | 1.43 | 0.230 |
| 109B | 4500 | 0.46 | 3700 | 1.22 | 21.95 | 33.79 | 43.37 | 323 | 244 | 1.32 | 0.229 |
| 111B | 4900 | 0.46 | 3700 | 1.32 | 22.67 | 33.33 | 43.73 | 345 | 265 | 1.30 | 0.228 |
| 114B | 6400 | 0.30 | 5650 | 1.13 | 22.73 | 31.10 | 46.74 | 371 | 235 | 1.58 | 0.253 |
| 115B | 7800 | 0.13 | 13050 | 0.60 | 23.91 | 33.66 | 43.12 | 560 | 389 | 1.44 | 0.295 |
| 116B | 6300 | 0.17 | 10000 | 0.63 | 22.94 | 32.91 | 43.88 | 409 | 299 | 1.37 | 0.255 |
| 117B | 5100 | 0.19 | 8950 | 0.57 | 22.18 | 33.68 | 43.48 | 347 | 267 | 1.30 | 0.255 |
| 118B | 5600 | 0.21 | 8100 | 0.69 | 21.30 | 34.63 | 43.46 | 618 | 381 | 1.62 | 0.335 |
| 120B | 6100 | 0.29 | 5850 | 1.04 | 22.96 | 33.48 | 44.11 | 292 | 249 | 1.18 | 0.230 |
| 121B | 5700 | 0.19 | 8950 | 0.64 | 22.78 | 32.95 | 43.52 | 593 | 442 | 1.34 | 0.355 |
| 122B | 4100 | 0.06 | 28000 | 0.14 | 22.57 | 34.18 | 41.35 | 630 | 405 | 1.55 | 0.080 |
| 124B | 4700 | 0.29 | 5850 | 0.80 | 21.11 | 35.66 | 42.76 | 295 | 226 | 1.30 | 0.135 |
| 126B | 6100 | 0.28 | 6050 | 1.01 | 24.27 | 32.18 | 43.65 | 266 | 235 | 1.13 | 0.182 |

b. (C) Comparison of Prepolymer Properties (U)

(U) The characterization data on the prepolymers of Series I and II are compared with one another and with two types of Butarez HT prepolymers (Lots 612 and 5593). The property values reported in Table VI were obtained from measurements or calculations made in these Laboratories. It is immediately obvious that the uniformity in properties of the prepolymers prepared in Series II is significantly greater than for similar properties of the prepolymers in Series I. This is attributed to the more constant initiator concentration used in Series II reactions. Prepolymers in both series displayed moderately high to extremely low values for their functionality. Many of the low values may reflect errors inherent in the analytical determinations of molecular weight and end-group content of the prepolymers. In most respects, the prepolymers of Series I and II are the equal (average basis) of the commercial Butarez HT prepolymers.

| Table VI. (U) Comparative Data for Series I and II Prepolymers | | | | |
|--|------------------|------------------|-------------------------|--------------------------|
| Property | Series I | Series II | Butarez HT (Lot-612) | Butarez HT (Lot-5593) |
| Gel Formation | 14 of 15 | 5 of 13 | - | - |
| Prepolymer Yields (%) | 67-94 | 88-99 | Good | Good |
| \bar{M}_n (V.P.O.) | 3700-14000 | 4100-7800 | 4100 | 3900 |
| Weight % OH | 0.05-0.71 | 0.06-0.49 | 0.53 | 0.42 |
| Equivalent Weight (OH) | 2400-34000 | 3700-28000 | 3210 | 4050 |
| Functionality | 0.11-1.72 (1.13) | 0.14-1.61 (0.88) | 1.28 | 0.96 |
| $[\eta]$ | 0.12-1.4 | 0.08-0.355 | - | - |
| Microstructure Cis-1,4 | ~19-20 | 21-23 | 21 | |
| (%) Trans-1,4 | ~38-42 | 42-44 | 42 | |
| Vinyl | ~34-36 | 32-34 | 30 ⁺ | |
| \bar{A}_w | 233-1880 | 266-630 | 341 | 357 |
| \bar{A}_n | 175-919 | 226-442 | 253 | 282 |
| PD | 1.30-2.57 | 1.18-1.62 | 1.35 | 1.27 |
| Cure Behavior | O.K. | - | O.K. | O.K. |

(C) Propellant compositions have been made successfully with prepolymers of Series I (98B, 99B, 102B, 103B, and 106B) and also with the Butarez HT prepolymers. The mechanical property data obtained on a number of compositions using Series I prepolymers are shown in Table VII. These data are preliminary, and it is pointed out that no attempt has yet been made to optimize the composition. It is apparent from these preliminary data that useful propellants can be obtained readily through the utilization of the prepolymers of Series I. Stress/strain data are given for an R-45M-based propellant, for comparative purposes. The propellant compositions were:

| | Propellant Composition (%) | Propellant Composition (%) |
|---|-------------------------------|-------------------------------|
| Binder | 9.91 | 9.60 |
| Ammonium Perchlorate (cc/cc 70/30 blend) | 70.64 | 70.64 |
| Aluminum (H-10) | 13.36 | 13.36 |
| Emolein ^a + Curative | 5.79 | 6.0 |
| MT-4 | 0.3 | 0.4 |

^a Trademark of Emery Industries, Inc., Cincinnati, Ohio.

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| Table VII. (C) Mechanical-Property Data on Propellants from Series I Prepolymers (U) | | | | |
|--|---------------------------|-----------------------|---------|-----------------------------------|
| Prepolymer No. | TDI/Prepolymer (gm/gm) | Mechanical Properties | | Stress/Strain at 140°F (psi/%) |
| | | -40°F | 77°F | |
| 98B | 0.419 | | 82/62 | |
| 99B | 0.480 | | 73/52 | |
| 102B | 0.414 | 217/84 | 64/49 | 57/96 |
| Blend { | 96B | 0.33 | No Cure | |
| | 98B | 0.43 | 133/45 | 22/76 |
| | 99B | 0.53 | 178/59 | 51/73 |
| | 102B | 0.63 | 297/47 | 73/26 |
| | 103B | 0.83 | No Cure | |
| 106B | 0.59 | | No Cure | |
| 106B | 0.79 | 473/12 | 180/12 | 144/12 |
| 106B | 0.89 | 440/17 | 171/14 | 149/16 |
| R-45M | - | 205/41 | 113/37 | 88/33 |

(U) No propellants have been made using the prepolymers of Series II; however, these materials are known to cure satisfactorily with a TDI LHT-240 curative system in gumstocks, and their usefulness in propellants remains to be demonstrated.

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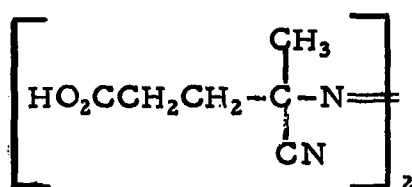
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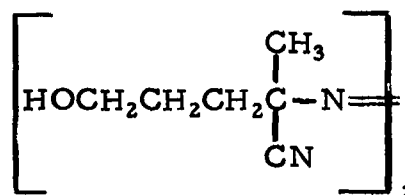
Section IV. (U) FREE RADICAL POLYMERIZATION

1. (U) General Comments

(U) The free radical polymerization of dienes with suitable functional group-containing azo initiators to yield HT- and CT-polydienes was a continuation of previous studies. The basic details of the experimental program were reported in an earlier report (3). It is important to point out that exclusive use was made of 4,4'-azo-bis(4-cyanovaleric acid) (AMCV) (I) from the Aldrich Chemical Company, or 4,4'-azo-bis(4-cyanopentanol) (AMHV) (II) prepared by the method of Bamford, et. al. (5) to initiate all free radical reactions.



I



II

2. (U) Results and Discussion of Free Radical Polymerization

(U) The major effect in the area of free radical polymerization was directed to the preparation of the prepolymers in sufficient quantities for propellant development studies. Prepolymers were prepared on a 100-gram scale for this purpose, and a concerted effort was directed to the preparation of HTPI and CTPI. It was of interest to ascertain the uniformity of properties of each type of prepolymers. Hence, a series of approximately 20 individual reactions for each type of prepolymer was completed and the prepolymer was characterized completely for comparative purposes. Subsequently, the prepolymers were blended according to type into a master batch for use in the propellant evaluation program.

(U) Associated polymerization studies were carried out on the preparation of CTPB and CTPI for use in methylation reactions leading to the development of an alternate method for obtaining the equivalent weight of the prepolymers. Details of this work will be reported elsewhere. The preparative work included the synthesis of a series of CTPB and CTPI prepolymers of varying molecular weights; characterization data on these two polymer series are described.

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(U) A series of CTPB prepolymers was prepared in three different solvents, dioxane, acetonitrile, and dimethylformamide (DMF), to examine the effect of solvent on the prepolymer properties. Since the prepolymers separate from solution when the polymerizations are carried out in acetonitrile or dimethylformamide, it was thought that the prepolymers from these particular reactions could possibly possess a lower molecular weight distribution than those prepolymers formed in dioxane, which is an excellent polydiene solvent. All prepolymers were characterized in detail.

(U) In another related area of the synthetic work, a series of polymerizations was conducted at temperatures varying from 40° to 80°C. The influence of temperature on the properties of the prepolymers was unknown; however, it was thought that perhaps the microstructure of the prepolymer could be altered to some extent by the polymerization temperature. Both butadiene and isoprene were investigated in this study.

(U) The characterization data for HTPB, HTPI, and HTPC prepolymers reported (3) previously have been extended to include nitrogen, intrinsic viscosity, microstructure, and molecular weight distribution determinations. The data are presented for reference purposes.

a. (U) Large-Scale Polymerization Reactions

(U) Large-scale polymerization reactions (100 gm) were carried out with butadiene and isoprene to give HTPB, CTPB, HTPI, and CTPI prepolymers. A series of reactions was completed for each type of prepolymer. Detailed characterization of all prepolymers was accomplished by the usual means (Tables VIII, IX, X, and XI). After analysis, the individual prepolymers were blended, according to type, into master batches for later use in propellant formulation studies. Special effort was given to the preparative effort on the HTPI and CTPI prepolymers.

(U) Characterization data for the HTPB prepolymers are presented in Table VIII. The first 9 reactions were performed for comparative purposes. Using the high-low values for most measured properties, it was found that the prepolymers were relatively uniform in character. This was particularly evident through a comparison of the nitrogen content and the calculated equivalent weights. Molecular weight values ranged from 2600 to 4300 consequently, and produced a relatively wide range of functionality values,

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whether calculated using the hydroxyl or the nitrogen content. Less uniformity was observed in the intrinsic viscosities, where the range appeared to vary beyond the desired limits. Little change was observed in the microstructure of the prepolymers as one would have expected. The ratio (percent) of cis-1,4:trans-1,4:vinyl was in the range of 16:61:23.

| Table VIII. (U) Characterization Data for HTPB Prepolymers - Large Scale Reactions [65°C - Dioxane-72 Hours-3 Mole % AMHV] | | | | | | | | | | | | |
|---|---------|-------------|-------------|------|-------------------|------|---------------|------|-------------------|-----------|-------|------------|
| FRB-No. | Yield % | \bar{M}_n | Weight % OH | % N | Equivalent Weight | | Functionality | | Microstructure, % | | | [η] |
| | | | | | OH | N | OH | N | Cis-1,4 | Trans-1,4 | Vinyl | |
| 224 | 66.5 | 4300 | 1.50 | 1.20 | 1130 | 1165 | 3.81 | 3.69 | 15.96 | 61.15 | 22.90 | 0.109 |
| 225 | 76.5 | 2600 | 1.54 | 1.24 | 1100 | 1130 | 2.36 | 2.30 | 16.65 | 60.22 | 23.13 | 0.137 |
| 226 | 67.5 | 2800 | 1.61 | 1.23 | 1055 | 1140 | 2.65 | 2.46 | 17.04 | 59.16 | 23.80 | 0.098 |
| 227 | 59.0 | 2700 | 1.60 | 1.25 | 1060 | 1120 | 2.55 | 2.41 | 17.41 | 59.71 | 22.88 | 0.114 |
| 228 | 54.0 | 3600 | 1.42 | 1.18 | 1195 | 1185 | 3.01 | 3.04 | ← I → | | | 0.132 |
| 236 | 63.0 | 2700 | 1.50 | 1.29 | 1130 | 1085 | 2.39 | 2.49 | 16.41 | 59.88 | 23.70 | 0.164 |
| 252 | 59.0 | 3600 | 1.17 | 1.09 | 1400 | 1285 | 2.57 | 2.80 | | | | 0.138 |
| 263 | 59.0 | 2600 | 1.41 | 1.15 | 1205 | 1215 | 2.16 | 2.14 | 16.83 | 60.14 | 23.03 | 0.172 |
| 264 | 59.0 | 3400 | 1.41 | 1.11 | 1205 | 1255 | 2.82 | 2.71 | 17.07 | 59.94 | 22.99 | 0.180 |
| 325 | 63.0 | 1900 | 2.24 | 1.95 | 760 | 715 | 2.50 | 2.66 | 16.96 | 60.91 | 22.13 | 0.132 |
| 331 | 65.0 | 2000 | 2.24 | 1.81 | 760 | 750 | 2.63 | 2.67 | 15.04 | 62.04 | 22.93 | 0.106 |
| 332 | - | 1900 | 2.13 | 1.94 | 800 | 720 | 2.38 | 2.64 | 17.70 | 60.44 | 21.86 | 0.077 |

(U) The last three reactions (Table VIII) showed the effect of increasing the initiator (AMHV) concentration from 3 to 10 mole percent. The major effects were to lower the molecular weight from an average value of 2000 and to lower the related intrinsic viscosities accordingly. A low equivalent weight also resulted from this action. Little change was observed in functionalities or microstructure, although it was expected that the functionality values would increase.

(U) Similar data are reported in Table IX for the CTPB prepolymers. The molecular weights of these prepolymers were significantly higher than those of the HTPB. Values ranged from a high of 8500 to a low of 3100. Other properties appeared to be comparable. It was also noted that higher initiator (AMCV)

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concentrations (10 mole %) affected the prepolymers by lowering their molecular weight, equivalent weight, and intrinsic viscosity, as expected.

| Table IX. (U) Characterization Data for CTPB Prepolymers - Large Scale Reactions [65°C -Dioxane-72 Hours-3 Mole % AMCV] | | | | | | | | | | | | |
|---|---------|-------------|------------|------|-------------------|------|-------------------|------|-------------------|-----------|-------|------------|
| FRB-No. | Yield % | \bar{M}_n | Weight %OH | %N | Equivalent Weight | | Functionality | | Microstructure, % | | | [η] |
| | | | | | CO ₂ H | N | CO ₂ H | N | Cis-1,4 | Trans-1,4 | Vinyl | |
| 274 | - | 3100 | 3.30 | 1.32 | 1365 | 1055 | 2.27 | 2.94 | 17.95 | 58.14 | 23.91 | 0.154 |
| 275 | 67.5 | 3500 | 3.42 | 1.30 | 1315 | 1075 | 2.66 | 3.25 | | | | 0.164 |
| 276 | 64.0 | 4400 | 3.11 | 1.21 | 1445 | 1155 | 3.04 | 3.81 | | | | 0.140 |
| 277 | 65.0 | 3500 | 3.18 | 1.19 | 1415 | 1175 | 2.47 | 2.98 | | | | 0.160 |
| 278 | 65.0 | 4800 | 3.35 | 1.15 | 1340 | 1220 | 3.58 | 3.93 | 16.66 | 59.65 | 23.69 | 0.184 |
| 279 | 75.0 | 4400 | 2.35 | 1.05 | 1915 | 1330 | 2.29 | 3.31 | 16.58 | 59.91 | 23.52 | 0.217 |
| 280 | 77.5 | 5300 | 2.81 | 1.05 | 1600 | 1330 | 3.31 | 3.99 | | | | 0.231 |
| 281 | 72.5 | 6200 | 3.09 | 1.06 | 1455 | 1320 | 4.26 | 4.70 | | | | 0.211 |
| 282 | 58.5 | 6200 | 3.24 | 1.13 | 1390 | 1245 | 4.46 | 4.98 | | | | 0.170 |
| 283 | 61.5 | 8500 | 3.20 | 1.09 | 1405 | 1285 | 6.05 | 6.62 | | | | 0.155 |
| 284 | 63.0 | 6400 | 3.32 | 1.14 | 1355 | 1230 | 4.72 | 5.20 | | | | 0.176 |
| 285 | 58.0 | 5200 | 3.17 | 1.06 | 1420 | 1320 | 3.66 | 3.94 | | | | 0.208 |
| 315 | 71.5 | 1100 | 6.21 | 2.59 | 725 | 540 | 1.52 | 2.04 | 19.37 | 56.60 | 24.03 | 0.138 |
| 326 | 74.0 | 1800 | 5.55 | 2.13 | 810 | 655 | 2.22 | 2.75 | 18.57 | 58.05 | 23.37 | 0.070 |
| 327 | 75.5 | 2000 | 5.78 | 2.19 | 780 | 640 | 2.56 | 3.12 | 19.42 | 57.28 | 21.12 | 0.070 |

(U) Data for the HTPI and CTPI prepolymers are reported in Tables X and XI. The prepolymer properties were similar in character to those observed for the polybutadienes. Obvious differences were noted in product yields. In most instances, lower yields were found for the polyisoprenes. Molecular weights of the HTPI prepolymers were lower than the CTPI.

b. (U) Prepolymers for Methylation

(U) A series of CTPB and CTPI prepolymers were prepared for methylation studies. It was of interest to obtain prepolymers of varying molecular weights for the methylation studies, since the methylated products were to be used in the development of a promising new method for equivalent weight determination.

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Characterization data for the prepolymers are displayed in Tables XII (CTPB) and XIII (CTPI). Initiator concentrations were varied from 0.5 to 5.0 mole percent to produce the prepolymers exhibiting molecular weights from about 2400 to 6500. The intrinsic viscosities of the prepolymers decreased in the expected order, and functionality values were usually in the range of 2 to 3. The molecular weight distribution (CTPI) appeared to decrease as the initiator concentration increased. This fact confirms the earlier reported results (3).

| Table X. (U) Characterization Data for HTPI Prepolymers - Large Scale Reactions [65°C - Dioxane - 72 Hours - 3 Mole % AMHV] | | | | | | | | | | | |
|--|-------------|----------------|------|-------------------|------|---------------|------|---------------|-------------|------|------------|
| FRB-No. | \bar{M}_n | Weight % OH | % N | Equivalent Weight | | Functionality | | G. P. C. Data | | | [η] |
| | | | | OH | N | OH | N | \bar{A}_w | \bar{A}_n | PD | |
| 359 | 2900 | 1.44 | 1.28 | 1180 | 1095 | 2.46 | 2.65 | 284 | 170 | 1.67 | 0.121 |
| 360 | 2600 | 1.37 | 1.34 | 1240 | 1045 | 2.26 | 2.68 | 272 | 153 | 1.78 | 0.120 |
| 361 | 2200 | 1.04 | 1.14 | 1635 | 1225 | 1.35 | 1.80 | 256 | 147 | 1.75 | |
| 362 | 2900 | 1.04 | 1.10 | 1635 | 1205 | 1.77 | 2.41 | 274 | 163 | 1.68 | |
| 363 | 2300 | 1.04 | 1.21 | 1635 | 1155 | 1.41 | 1.99 | 242 | 145 | 1.67 | |
| 367 | 2800 | 1.54 | 1.49 | 1105 | 940 | 2.53 | 2.98 | 221 | 141 | 1.57 | 0.130 |
| 368 | 1500 | 1.33 | 1.12 | 1280 | 1250 | 1.17 | 1.20 | 224 | 132 | 1.70 | 0.122 |
| 369 | 2400 | 1.33 | 1.19 | 1280 | 1175 | 1.87 | 2.04 | 227 | 134 | 1.70 | 0.124 |
| 370 | 2400 | 1.39 | 1.23 | 1220 | 1140 | 1.97 | 2.11 | 233 | 132 | 1.76 | 0.124 |
| 371 | 2500 | 1.52 | 1.32 | 1120 | 1060 | 2.23 | 2.36 | 215 | 135 | 1.60 | 0.122 |
| 372 | 2700 | 1.34 | 1.30 | 1270 | 1075 | 2.13 | 2.51 | 239 | 142 | 1.68 | 0.115 |
| 373 | 2500 | 1.49 | 1.41 | 1140 | 995 | 2.19 | 2.51 | 230 | 136 | 1.69 | 0.138 |
| | 2800 | 1.47 | 1.39 | 1155 | 1005 | 2.42 | 2.79 | 217 | 127 | 1.70 | 0.143 |
| 375 | 2600 | 1.46 | 1.37 | 1165 | 1020 | 2.23 | 2.55 | 208 | 123 | 1.69 | 0.108 |
| 377 | 3000 | 1.16 | 1.16 | 1465 | 1205 | 2.05 | 2.49 | 248 | 154 | 1.60 | 0.101 |
| 378 | 3200 | 1.16 | 1.27 | 1465 | 1110 | 2.18 | 2.88 | 223 | 146 | 1.53 | 0.068 |
| 379 | 3300 | 0.96 | 1.17 | 1810 | 1195 | 1.82 | 2.76 | 206 | 139 | 1.49 | 0.077 |
| 380 | 2700 | 1.11 | 1.21 | 1530 | 1155 | 1.76 | 2.34 | 243 | 148 | 1.64 | 0.098 |
| 381 | 3300 | 1.12 | 1.17 | 1520 | 1195 | 2.30 | 2.93 | 222 | 149 | 1.49 | 0.117 |
| 382 | 2900 | 1.05 | 1.13 | 1620 | 1240 | 1.79 | 2.34 | 242 | 146 | 1.65 | 0.136 |
| 383 | 2700 | 1.11 | 1.15 | 1530 | 1215 | 1.76 | 2.22 | 229 | 133 | 1.72 | 0.060 |
| 384 | 2800 | 1.21 | 1.24 | 1405 | 1130 | 1.99 | 2.48 | 228 | 134 | 1.71 | 0.115 |

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| Table XI. (U) Characterization Data for CTPI Prepolymers - Large Scale Reactions [65°C - Dioxane - 72 Hours - 3 Mole % AMCV] | | | | | | | | | | | |
|---|-------------|-------------------------------|------|-------------------|------|-------------------|------|---------------|-------------|------|------------|
| FRB-No. | \bar{M}_n | Weight % CO ₂ H | % N | Equivalent Weight | | Functionality | | G. P. C. Data | | | [η] |
| | | | | CO ₂ H | N | CO ₂ H | N | \bar{A}_w | \bar{A}_n | PD | |
| 286 | 4100 | 3.39 | 1.21 | 1325 | 1155 | 3.09 | 3.55 | - | - | - | - |
| 287 | 3700 | 3.18 | 1.14 | 1415 | 1230 | 2.61 | 3.01 | 253 | 146 | 1.74 | - |
| 288 | 4800 | 3.09 | 1.15 | 1455 | 1215 | 2.32 | 3.87 | 256 | 155 | 1.67 | - |
| 289 | 4800 | 3.09 | 1.21 | 1455 | 1155 | 3.30 | 4.16 | 231 | 140 | 1.65 | - |
| 290 | 2100 | 3.45 | 1.33 | 1305 | 1055 | 1.61 | 1.99 | 219 | 137 | 1.60 | - |
| 291 | 2400 | 3.51 | 1.31 | 1280 | 1070 | 1.88 | 2.24 | 229 | 139 | 1.64 | - |
| 292 | 2300 | 3.56 | 1.31 | 1265 | 1070 | 1.82 | 2.15 | 196 | 127 | 1.54 | - |
| 386 | 2600 | | 1.47 | | 955 | | 2.72 | 166 | 114 | 1.45 | 0.095 |
| 387 | 2600 | | 1.52 | | 920 | | 2.83 | 183 | 127 | 1.45 | 0.080 |
| 388 | 2800 | | 1.39 | | 1005 | | 2.79 | | | | 0.096 |
| 389 | 3800 | 2.55 | 1.09 | 1765 | 1285 | 2.15 | 2.96 | 241 | 142 | 1.69 | 0.115 |
| 390 | 3400 | 2.88 | 1.13 | 1565 | 1240 | 2.17 | 2.74 | 231 | 141 | 1.64 | 0.138 |
| 391 | 3700 | 3.14 | 1.11 | 1435 | 1255 | 2.58 | 2.95 | 233 | 142 | 1.64 | 0.130 |
| 392 | 3700 | 3.23 | 1.21 | 1390 | 1155 | 2.66 | 3.20 | 213 | 142 | 1.50 | 0.150 |
| 393 | 4100 | 3.46 | 1.20 | 1300 | 1165 | 3.15 | 3.52 | 211 | 143 | 1.48 | 0.118 |
| 394 | 4300 | 3.40 | 1.16 | 1320 | 1205 | 3.26 | 3.57 | 218 | 142 | 1.54 | 0.112 |
| 395 | 3700 | 3.28 | 1.17 | 1370 | 1195 | 2.70 | 3.10 | 234 | 143 | 1.64 | 0.120 |
| 396 | 4200 | 3.23 | 1.21 | 1390 | 1155 | 3.02 | 3.64 | 237 | 140 | 1.70 | 0.120 |
| 397 | 4200 | 3.28 | 1.15 | 1370 | 1215 | 3.07 | 3.46 | 223 | 141 | 1.58 | 0.120 |
| 398 | 3800 | | | | | | | 239 | 145 | 1.65 | 0.278 |
| 399 | 4000 | | | | | | | 256 | 158 | 1.62 | 0.284 |
| 401 | 4300 | 3.47 | 1.23 | 1295 | 1135 | 3.32 | 3.79 | 212 | 133 | 1.60 | 0.120 |
| 402 | 4300 | 3.42 | 1.13 | 1315 | 1240 | 3.04 | 3.23 | 229 | 143 | 1.60 | 0.121 |
| 403 | 3800 | 3.26 | 1.13 | 1380 | 1240 | 2.75 | 3.06 | 213 | 135 | 1.57 | 0.120 |
| 404 | 3000 | 2.45 | 1.21 | 1835 | 1155 | 1.63 | 2.60 | 213 | 133 | 1.60 | 0.119 |
| 405 | 3800 | 2.68 | 1.21 | 1680 | 1155 | 2.26 | 3.29 | 231 | 142 | 1.63 | 0.124 |
| 406 | 3400 | 3.19 | 1.28 | 1410 | 1095 | 2.41 | 3.11 | 233 | 140 | 1.67 | 0.132 |
| 407 | 3400 | 2.81 | 1.22 | 1600 | 1150 | 2.13 | 2.96 | 226 | 137 | 1.65 | 0.124 |
| 408 | 3900 | 2.95 | 1.20 | 1525 | 1165 | 2.56 | 3.35 | 245 | 148 | 1.66 | 0.116 |

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| Table XII. (U) Characterization Data for CTPB Prepolymers - Prepared for Methylation [65°C - Dioxane - 72 Hours] | | | | | | | | | | | | |
|---|----------------|-------------|-------------------------------|------|-------------------|------|-------------------|------|-------------------|-----------|-------|------------|
| FRB-No. | Mole % AMCV | \bar{M}_n | Weight % CO ₂ H | %N | Equivalent Weight | | Functionality | | Microstructure, % | | | [η] |
| | | | | | CO ₂ H | N | CO ₂ H | N | Cis-1,4 | Trans-1,4 | Vinyl | |
| 297 | 0.5 | 6500 | 0.73 | 0.47 | 2325 | 2820 | 2.80 | 2.30 | | | | 0.334 |
| 298 | 1.0 | 4600 | 0.96 | 0.47 | 1760 | 2820 | 2.61 | 1.63 | 16.04 | 60.96 | 23.00 | 0.313 |
| 299 | 2.0 | 5300 | 1.19 | 0.68 | 1430 | 2030 | 3.70 | 2.62 | 16.69 | 60.73 | 22.58 | 0.208 |
| 300 | 3.0 | 3800 | 1.85 | 1.09 | 920 | 1285 | 4.13 | 2.96 | 16.54 | 60.70 | 22.76 | 0.192 |

| Table XIII. (U) Characterization Data for CTPI Prepolymers - Prepared for Methylation [65°C - Dioxane - 72 Hours] | | | | | | | | | | | | |
|--|----------------|-------------|-------------------------------|------|-------------------|------|-------------------|------|---------------|-------------|------|------------|
| FP | Mole % AMCV | \bar{M}_n | Weight % CO ₂ H | %N | Equivalent Weight | | Functionality | | G. P. C. Data | | | [η] |
| | | | | | CO ₂ H | N | CO ₂ H | N | \bar{A}_w | \bar{A}_n | PD | |
| 421 | 0.5 | 6300 | 1.27 | 0.59 | 3540 | 2375 | 1.78 | 2.65 | 239 | 142 | 1.62 | 0.237 |
| 422 | 1.0 | 5600 | 1.61 | 0.69 | 2790 | 2030 | 2.01 | 2.76 | 361 | 189 | 1.91 | 0.196 |
| 423 | 2.0 | 4300 | 2.33 | 0.99 | 1930 | 1415 | 2.22 | 3.04 | 258 | 156 | 1.65 | 0.110 |
| 424 | 3.0 | 3700 | 2.70 | 1.08 | 1670 | 1295 | 2.22 | 2.86 | 199 | 140 | 1.42 | 0.070 |
| 425 | 5.0 | 2400 | 3.73 | 1.89 | 1205 | 740 | 1.99 | 3.24 | 140 | 113 | 1.24 | 0.075 |

c. (U) Solvent Effects

(U) It had been noted earlier that when the dienes were polymerized in polar solvents such as acetonitrile or dimethylformamide (DMF), the polymer produced in the reaction separated from the solution to give a two-phase liquid system. The possible use of this phenomenon to aid in the free radical synthesis of polydienes exhibiting a low-molecular weight distribution was of interest to the polymer synthesis program. A series of polymerizations of butadiene were performed in dioxane, acetonitrile, and DMF to confirm experimentally that the product separating from solution (acetonitrile, DMF) was indeed one possessing a low polydispersity. The results of the characterization of the prepolymers (Table XIV) show that the polydispersity (PD) remains essentially unchanged regardless of the solvent and whether or not the product remains in solution or separate from solution during the reaction. Compare PD

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values of prepolymers prepared in the different solvents at similar initiator (AMCV) concentrations. Little change is noted. Again, the initiator concentration was an important factor in determining the PD of the prepolymers. The effects of solvent were very limited, with the most observable effect being its influence on molecular weight. Prepolymers prepared in dioxane (good solvent for polymer) had higher molecular weights and intrinsic viscosities than those prepared in acetonitrile (poor solvents for polymer). No change was noted in the prepolymer's microstructure.

| Table XIV. (U) Characterization Data for CTPB Prepolymers - Solvent Effect [65°C - 72 Hours - AMCV] | | | | | | | | | | | | | | | | |
|--|---------|-------------|-------------|----------------------------|------|-------------------|------|-------------------|------|-------------------|-----------|-------|---------------|-------------|------|------------|
| CT-No. | Yield % | Mole % AMCV | \bar{M}_n | Weight % CO ₂ H | %N | Equivalent Weight | | Functionality | | Microstructure, % | | | G. P. C. Data | | | [η] |
| | | | | | | CO ₂ H | N | CO ₂ H | N | Cis-1,4 | Trans-1,4 | Vinyl | \bar{A}_w | \bar{A}_n | PD | |
| <u>DIOXANE</u> | | | | | | | | | | | | | | | | |
| 29 | 30 | 0.5 | 6500 | 1.26 | 0.53 | 3575 | 2640 | 1.82 | 2.46 | ← I → | | | 823 | 415 | 1.98 | 0.420 |
| 3 | 59 | 3.0 | 3100 | 3.15 | 1.31 | 1430 | 1070 | 2.17 | 2.90 | 16.96 | 58.90 | 21.89 | 258 | 171 | 1.51 | 0.290 |
| 30 | 53 | 10.0 | 2200 | 4.70 | 1.78 | 960 | 785 | 2.29 | 2.80 | 19.38 | 57.72 | 22.90 | 143 | 125 | 1.15 | 0.125 |
| <u>ACETONITRILE</u> | | | | | | | | | | | | | | | | |
| 139 | 8.5 | 0.5 | 3400 | 2.45 | 1.01 | 1835 | 1385 | 1.85 | 2.45 | ← I → | | | 291 | 177 | 1.64 | 0.200 |
| 140 | 38 | 3.0 | 2600 | 3.53 | 1.31 | 1275 | 1070 | 2.04 | 2.43 | 16.82 | 59.68 | 23.50 | 198 | 141 | 1.41 | 0.148 |
| 141 | 43 | 5.0 | 2400 | 4.35 | 1.66 | 1035 | 845 | 2.32 | 2.84 | 18.58 | 57.87 | 23.55 | 151 | 113 | 1.33 | 0.108 |
| 142 | 46 | 10.0 | 1500 | 4.99 | 2.05 | 900 | 680 | 1.67 | 2.21 | 18.77 | 57.52 | 23.71 | 116 | 99 | 1.17 | 0.090 |
| <u>DIMETHYLFORMAMIDE</u> | | | | | | | | | | | | | | | | |
| 98 | 26 | 0.5 | 6300 | 1.61 | 0.64 | 2795 | 2190 | 2.25 | 2.88 | 15.19 | 60.19 | 24.62 | 608 | 299 | 2.03 | 0.298 |
| 96 | 55 | 3.0 | 4800 | 2.84 | 1.09 | 1585 | 1285 | 3.03 | 3.74 | 13.66 | 62.50 | 23.84 | 249 | 171 | 1.46 | 0.200 |
| 97 | 30 | 5.0 | 2250 | 3.16 | 1.28 | 1425 | 1095 | 1.58 | 2.05 | 15.68 | 60.43 | 23.89 | 213 | 158 | 1.35 | 0.150 |

d. (U) Polymerization Temperature Effect

(U) An investigation of the effect of the polymerization temperature on the properties of the polydienes was carried out in reactions leading to the preparation of HTPB and HTPI prepolymers. Interest in this study centered on the possibility that the microstructure of the prepolymers could be altered by appropriate changes in reaction temperature. Polymerizations were conducted in duplicate at temperatures of 40°, 50°, 60°, 70°, and 80°C with butadiene and isoprene initiated with 3 mole % AMHV in dioxane. Tables XV and XVI contain the characterization data on these prepolymers.

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| Table XV. (U) Characterization Data for HTPB Prepolymers - Polymerisation Temperature Effect [Dioxane - 72 Hours - 3 Mole % AMHV] | | | | | | | | | | | | | | | | |
|--|--------------|-------------|-------------|---------------|------|-------------------|------|---------------|------|-------------------|-----------|-------|---------------|-------------|------|------------|
| FRB-No. | Temp., °C | Yield, % | \bar{M}_n | Weight %OH | %N | Equivalent Weight | | Functionality | | Microstructure, % | | | G. P. C. Data | | | [η] |
| | | | | | | OH | N | OH | N | Cis-1,4 | Trans-1,4 | Vinyl | \bar{A}_w | \bar{A}_n | PD | |
| 417 | 40 | 33 | 4300 | 0.95 | 0.86 | 1790 | 1625 | 2.40 | 2.65 | - | - | - | 293 | 218 | 1.34 | 0.150 |
| 418 | 40 | 24 | 4400 | 0.64 | 0.82 | 2655 | 1705 | 1.66 | 2.58 | 12.84 | 64.54 | 22.62 | 270 | 214 | 1.26 | 0.168 |
| 431 | 50 | 48 | 3600 | 1.15 | 0.93 | 1480 | 1505 | 2.43 | 2.39 | 15.19 | 61.70 | 23.12 | 211 | 171 | 1.24 | 0.134 |
| 432 | 50 | 50 | 3800 | 1.22 | 0.99 | 1395 | 1415 | 2.72 | 2.69 | 15.25 | 61.47 | 23.28 | 245 | 192 | 1.27 | 0.146 |
| 413 | 60 | 50 | 3300 | 1.29 | 1.12 | 1320 | 1295 | 2.50 | 2.55 | 16.45 | 61.10 | 22.45 | 192 | 158 | 1.21 | 0.118 |
| 414 | 60 | 50 | 3600 | 1.29 | 1.10 | 1320 | 1250 | 2.72 | 2.88 | 16.20 | 60.98 | 22.82 | 191 | 156 | 1.23 | 0.131 |
| 409 | 70 | 44 | 3700 | 0.90 | 0.87 | 1895 | 1610 | 1.95 | 2.30 | 17.32 | 59.64 | 23.04 | 367 | 187 | 1.96 | 0.216 |
| 410 | 70 | 43 | 3500 | 0.94 | 0.87 | 1810 | 1610 | 1.93 | 2.17 | 17.41 | 57.68 | 25.04 | 442 | 220 | 2.01 | 0.202 |
| 435 | 80 | 23 | 3300 | 1.24 | 0.99 | 1370 | 1415 | 2.41 | 2.33 | 17.84 | 59.03 | 23.13 | 326 | 173 | 1.89 | 0.213 |
| 436 | 80 | 35 | 3000 | 1.32 | 1.04 | 1285 | 1345 | 2.33 | 2.23 | 17.65 | 58.83 | 23.53 | 230 | 160 | 1.44 | 0.134 |

| Table XVI. (U) Characterisation Data for HTPB Prepolymers - Polymerisation Temperature Effect [Dioxane - 72 Hours - 3 Mole % AMHV] | | | | | | | | | | | | | | | | |
|---|--------------|-------------|-------------|---------------|------|-------------------|------|---------------|------|-------------------|-----------|-----------|---------------|-------------|------|------------|
| FRB-No. | Temp., °C | Yield, % | \bar{M}_n | Weight %OH | % N | Equivalent Weight | | Functionality | | Microstructure, % | | | G. P. C. Data | | | [η] |
| | | | | | | OH | N | OH | N | Cis-1,4 | Vinyl-1,2 | Vinyl-3,4 | \bar{A}_w | \bar{A}_n | PD | |
| 419 | 40 | 12 | 3900 | | | | | | | - | - | - | 225 | 178 | 1.27 | |
| 420 | 40 | 10 | 4300 | 0.64 | | 2605 | | 1.65 | | 78.28 | 14.62 | 7.10 | 226 | 181 | 1.25 | 0.284 |
| 433 | 50 | 30 | 4100 | 1.26 | 1.02 | 1349 | 1370 | 3.03 | 2.99 | 77.40 | 15.05 | 7.55 | 175 | 146 | 1.20 | 0.072 |
| 434 | 50 | 30 | 3700 | 1.20 | 0.99 | 1415 | 1410 | 2.61 | 2.62 | 77.07 | 15.41 | 7.51 | 188 | 154 | 1.23 | 0.192 |
| 415 | 60 | 36 | 3700 | 1.25 | 1.10 | 1360 | 1270 | 2.72 | 2.91 | 77.67 | 14.87 | 7.44 | 173 | 136 | 1.27 | 0.138 |
| 416 | 60 | 29 | 3600 | 1.30 | 1.10 | 1305 | 1270 | 2.76 | 2.63 | 77.19 | 15.31 | 7.50 | 155 | 132 | 1.18 | 0.100 |
| 411 | 70 | 34 | 3400 | 1.06 | 1.07 | 1605 | 1285 | 2.12 | 2.65 | 77.63 | 14.73 | 7.63 | 254 | 149 | 1.70 | 0.066 |
| 412 | 70 | 36 | 3600 | 1.05 | 1.08 | 1620 | 1310 | 2.22 | 2.75 | 77.79 | 14.84 | 7.37 | 242 | 145 | 1.67 | 0.120 |
| 437 | 80 | 27 | 3600 | 1.22 | 1.08 | 1390 | 1295 | 2.59 | 2.78 | 75.62 | 17.00 | 7.38 | | | | 0.149 |
| 438 | 80 | 35 | 2900 | 1.28 | 1.08 | 1325 | 1295 | 2.19 | 2.24 | 77.02 | 15.24 | 7.74 | 206 | 137 | 1.50 | 0.073 |

(U) The HTPB prepolymers prepared in duplicate runs at any given temperature displayed quite similar properties in most areas. No significant difference in the microstructure was apparent on comparison of the experimental data. The ratio of cis-1,4:trans-1,4:vinyl was about 16:61:23, as found previously for most reaction products prepared at 65°C. Other properties of these prepolymers were also similar (molecular weights, functionalities, etc.) except for the G. P. C. data.

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(U) It was immediately apparent that the prepolymers prepared at the lower temperatures possessed PD quite lower in value than those prepared at the higher temperatures. The natural break came in the temperature range between 60° and 70°C. All prepolymers formed in reactions at 60°C and below showed PD values of 1.3 or less, while those prepared at 70°C or above had PD values of 1.4 or greater. It is assumed that the normal reaction temperature of 65°C is on the high PD scale, since all reactions carried out at 65°C with 3 moles of AMHV gave a prepolymer with a PD value greater than 1.5.

(U) Similar behavior in the PD values was observed for the HTPI prepolymers (Table XVII) with the sharp break in high-low values coming between 60° and 70°C reactions. Other properties of the HTPI prepolymers were found similar to those reported for prepolymers prepared at 65°C.

| Table XVII. (U) Characterization Data for HTPB Prepolymers - Experimental Study | | | | | | | | | | | | | | | | | |
|---|-----------|---------------------|-----------|-------------|-------------|------|-------------------|------|---------------|------|--------------------|-----------|-------|-------------|-------------|------|------------|
| [65°C - 3 Mole % AMHV] | | | | | | | | | | | | | | | | | |
| FRB-No. | Time (Hr) | Solvent Volume (ml) | Yield (%) | \bar{M}_n | Weight % OH | % N | Equivalent Weight | | Functionality | | Microstructure (%) | | | G.P.C. Data | | | [η] |
| | | | | | | | OH | N | OH | N | Cis-1,4 | Trans-1,4 | Vinyl | \bar{A}_w | \bar{A}_n | PD | |
| DIOXANE | | | | | | | | | | | | | | | | | |
| 229 | 72 | 40 | 46.0 | 3100 | 1.35 | 1.08 | 1260 | 1300 | 2.46 | 2.38 | 18.04 | 59.55 | 23.40 | 300 | 189 | 1.59 | 0.200 |
| 230 | 72 | 20 | 51.5 | 3000 | 1.31 | 1.03 | 1300 | 1360 | 2.31 | 2.21 | 16.45 | 60.02 | 23.40 | 362 | 200 | 1.81 | 0.286 |
| 231 | 72 | 10 | 51.5 | 3700 | 1.33 | 0.98 | 1275 | 1430 | 2.90 | 2.59 | 15.70 | 61.72 | 22.59 | 407 | 220 | 1.85 | 0.296 |
| TOLUENE | | | | | | | | | | | | | | | | | |
| 232 | 72 | 40 | 33.0 | 2500 | 1.37 | 1.05 | 1240 | 1330 | 2.02 | 1.80 | ← I → | | | 451 | 206 | 2.19 | 0.260 |
| 233 | 72 | 20 | 35.0 | 3900 | 1.45 | 0.86 | 1170 | 1625 | 3.33 | 2.40 | 16.30 | 60.98 | 22.72 | 425 | 222 | 1.91 | 0.310 |
| 234 | 72 | 10 | 32.0 | 5000 | 1.19 | 0.75 | 1430 | 1870 | 3.50 | 2.67 | 15.59 | 61.55 | 22.86 | 559 | 276 | 2.03 | 0.350 |
| TOLUENE | | | | | | | | | | | | | | | | | |
| 237 | 24 | 30 | 27.0 | 2400 | 1.23 | 1.07 | 1370 | 1305 | 1.75 | 1.84 | 16.10 | 60.33 | 23.57 | 251 | 186 | 1.35 | 0.184 |
| 238 | 48 | 30 | 36.0 | 2300 | 1.21 | 0.98 | 1405 | 1430 | 1.64 | 1.61 | 16.64 | 60.56 | 22.79 | 399 | 230 | 1.73 | 0.205 |
| 239 | 120 | 30 | 38.0 | 3500 | 1.03 | 0.90 | 1650 | 1555 | 2.12 | 2.25 | 17.09 | 60.89 | 22.02 | 436 | 228 | 1.91 | 0.434 |

e. (U) Further Characterization of HT-Polydienes

(U) The characterization of HT-polydienes has been extended to include nitrogen, intrinsic viscosity, micro-structure, and some molecular weight distribution analysis. The data (Tables XVII, XVIII, and XIX) are given for HTPB, HTPI, and HTPC, and are included for reference purposes.

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| Table XVIII. (U) Characterization Data for HTPI Prepolymers - Experimental Study | | | | | | | | | | | | | | |
|--|-----------|---------------------|-----------|-------------|-------------|------|-------------------|------|---------------|------|--------------------|-----------|-----------|------------|
| [65 °C - 3 Mole % AMHV] | | | | | | | | | | | | | | |
| FRB-No. | Time (Hr) | Solvent Volume (ml) | Yield (%) | \bar{M}_n | Weight % OH | % N | Equivalent Weight | | Functionality | | Microstructure (%) | | | [η] |
| | | | | | | | OH | N | OH | N | Cis-1,4 | Vinyl-1,2 | Vinyl-3,4 | |
| DIOXANE | | | | | | | | | | | | | | |
| 243 | 72 | 40 | 32.0 | 2400 | 1.16 | 1.08 | 1465 | 1295 | 1.64 | 1.85 | 76.81 | 15.73 | 7.46 | 0.125 |
| 244 | 72 | 20 | 36.0 | 2800 | 1.11 | 0.99 | 1530 | 1415 | 1.83 | 1.98 | 77.83 | 14.75 | 7.43 | 0.158 |
| 245 | 72 | 10 | 43.0 | 4500 | 1.07 | 0.97 | 1590 | 1495 | 2.83 | 3.01 | 77.44 | 15.16 | 7.40 | 0.153 |
| TOLUENE | | | | | | | | | | | | | | |
| 248 | 72 | 40 | 26.0 | 3900 | 1.28 | 1.04 | 1325 | 1395 | 2.94 | 2.80 | 77.64 | 14.99 | 7.37 | 0.109 |
| 249 | 72 | 20 | 24.0 | 4500 | 1.11 | 0.96 | 1530 | 1460 | 2.94 | 3.08 | 77.64 | 15.08 | 7.28 | 0.120 |
| 250 | 72 | 10 | 28.0 | 2200 | 0.90 | 0.81 | 1890 | 1730 | 1.16 | 1.27 | 77.33 | 15.24 | 7.43 | 0.168 |
| TOLUENE | | | | | | | | | | | | | | |
| 240 | 24 | 30 | 20.0 | 2700 | 1.21 | 1.00 | 1380 | 1400 | 1.96 | 1.93 | 78.84 | 14.34 | 7.23 | 0.125 |
| 241 | 48 | 30 | 27.0 | 2500 | 1.19 | 0.98 | 1405 | 1430 | 1.78 | 1.75 | 77.53 | 14.95 | 7.53 | 0.156 |
| 242 | 120 | 30 | 29.0 | 3700 | 0.96 | 0.86 | 1770 | 1625 | 2.09 | 2.28 | 77.98 | 14.64 | 7.38 | 0.209 |

| Table XIX. (U) Characterization Data for HTPC Prepolymers - Experimental Study | | | | | | | | | | |
|--|-----------|---------------------|-----------|-------------|-------------|------|-------------------|------|---------------|------|
| [65°C - 3 Mole % AMHV] | | | | | | | | | | |
| FRB-No. | Time (Hr) | Solvent Volume (ml) | Yield (%) | \bar{M}_n | Weight % OH | % N | Equivalent Weight | | Functionality | |
| | | | | | | | OH | N | OH | N |
| DIOXANE | | | | | | | | | | |
| 253 | 72 | 40 | 77.4 | 8400 | 0.66 | 0.50 | 2575 | 2800 | 3.26 | 3.00 |
| 270 | 72 | 30 | 87.6 | 4500 | 0.60 | 0.64 | 2885 | 2185 | 1.56 | 2.06 |
| 254 | 72 | 20 | 81.9 | 9700 | 0.59 | 0.48 | 2880 | 2920 | 3.37 | 3.32 |
| 255 | 72 | 10 | 84.2 | 10800 | 0.52 | 0.59 | 3270 | 2370 | 3.06 | 4.21 |
| TOLUENE | | | | | | | | | | |
| 256 | 72 | 40 | 82.5 | 7500 | 0.60 | 0.55 | 2830 | 2590 | 2.65 | 2.89 |
| 257 | 72 | 20 | 81.9 | 6300 | 0.49 | 0.46 | 3470 | 3040 | 1.82 | 2.07 |
| 258 | 72 | 10 | 85.3 | 7500 | 0.42 | 0.44 | 3620 | 3180 | 2.07 | 2.36 |
| DIOXANE | | | | | | | | | | |
| 260 | 24 | 30 | 86.4 | 5400 | 0.46 | 0.49 | 3695 | 2860 | 1.46 | 1.89 |
| 263 | 48 | 30 | 58.0 | 3900 | 0.59 | | 2880 | | 0.89 | |
| 262 | 72 | 30 | 85.3 | 3900 | 0.39 | 0.43 | 4360 | 3255 | 0.89 | 1.25 |
| 261 | 120 | 30 | 86.4 | 2800 | 0.48 | 0.60 | 3540 | 2380 | 0.79 | 1.18 |
| TOLUENE | | | | | | | | | | |
| 265 | 24 | 30 | 84.8 | 5300 | 0.39 | 0.45 | 4360 | 3110 | 1.22 | 1.70 |
| 266 | 48 | 30 | 79.1 | 3000 | 0.41 | 0.45 | 4145 | 3110 | 0.72 | 0.96 |
| 267 | 72 | 30 | 88.7 | 5500 | 0.56 | 0.43 | 3030 | 3255 | 1.82 | 1.69 |
| 259 | 120 | 30 | 86.4 | 8600 | 0.35 | 0.47 | 4850 | 2980 | 1.77 | 2.89 |

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(U) REFERENCES

1. Fethers, L. J., J. Research National Bureau of Standards, A Physics and Chemistry, 70A, No. 5, 421 (1966).
2. Rohm and Haas Company, Huntsville, Alabama 35807, THE SYNTHESIS OF HTPB PREPOLYMERS BY ANIONIC POLYMERIZATION METHODS, S. F. Reed, Jr., November 1968, Technical Report S-185, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809, Contracts DAAH01-67-C-0655 and DAAH01-68-C-0632 (Unclassified) AD 843 923.
3. Rohm and Haas Company, Huntsville, Alabama 35807, CONJUGATED DIENE POLYMERS FOR SOLID PROPELLANTS, S. F. Reed, Jr., January 1969, Technical Report S-196, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809, Contract DAAH01-68-C-0632 (Confidential) AD 395 215 L.
4. Kamienski, C. W., Diesing, A. C., and Morrison, R. C. B., U. S. Patent, 3,388, 178, June 11, 1968.
5. Bamford, C. H., Jenkins, A. D., and Wayne, R. P., Trans. Faraday Soc., 56, 923 (1960).

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| 13. ABSTRACT <p>This report describes the synthesis and characterization of polybutadienes and polyisoprenes possessing hydroxyl and/or carboxyl functionality. Polymer formation was accomplished through anionic or free radical initiated reactions. Characterization of the materials involved analyses for molecular weight, molecular weight distribution, microstructure, end-group content, and solution viscosity. The objectives of the program were to scale up the anionic polymerization of butadiene to produce a superior HTPB prepolymer, and to prepare by free radical techniques superior HTPB as well as hydroxyl- and carboxyl-terminated isoprene polymers for solid propellant binders.</p> <p>Large-scale (100 gm) anionic polymerization of butadiene was carried out with two different dilithio initiators. A prepolymer (HTPB) exhibiting greater uniformity in properties was obtained with a commercial initiator than with an initiator prepared in-house. Functionality of the HTPB prepolymer ranged from 1.7 to 0.1 with average values near 1.0. In most respects these materials were comparable to similar commercial prepolymers. Preliminary gum stock and propellant development studies with the prepolymer confirmed their suitability as propellant binders.</p> <p>Free radical polymerizations of butadiene and isoprene were carried out to give sufficient quantities of prepolymers for propellant development studies. Emphasis was focused on the preparation of HTPI and CTPI because the cis-1,4 form of</p> | | |

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| KEY WORDS | LINK A | | LINK B | | LINK C | |
|--|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Polymerization | | | | | | |
| Anionic | | | | | | |
| Free Radical | | | | | | |
| Functionally-terminated | | | | | | |
| Dienes | | | | | | |
| Polybutadiene | | | | | | |
| Polyisoprene | | | | | | |
| Polychloroprene | | | | | | |
| Molecular weight | | | | | | |
| Molecular weight distribution | | | | | | |
| Viscosity | | | | | | |
| Functionality | | | | | | |
| Propellants | | | | | | |
| Microstructure | | | | | | |
| Synthesis | | | | | | |
| Properties | | | | | | |
| Initiators | | | | | | |
| Abstract (Continued) | | | | | | |
| <p>polymer should lead to favorable low-temperature properties of these materials. Polymerizations carried out in various solvents demonstrated that the solvent has little effect on properties of the prepolymer. An important discovery was that the polymerization temperature plays an important part in determining the molecular weight distribution of prepolymers formed in free radical polymerizations. Reactions leading to HTPB or HTPI conducted at 60°C or lower exhibited a polydispersity of 1.3 or less.</p> | | | | | | |

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Sent: Tuesday, March 13, 2001 11:01 AM
To: 'Downing, Lawrence'
Subject: RE: AD-506894, Question on Distribution Limitation

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The document to which you refer:

AD-506894 Jan 1970. Technical Report: S-242
"Synthesis of HTPB and CTPB Prepolymers by Anionic and Free-Radical
Polymerization"

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-----Original Message-----

From: Downing, Lawrence [mailto:ldowning@dtic.mil]
Sent: Tuesday, March 13, 2001 9:57 AM
To: 'mike.lyon@redstone.army.mil'
Cc: Kramer, Anna; Briggs, June
Subject: AD-506894, Question on Distribution Limitation

Mr. Lyon,

Request confirmation that AD-506894 is distribution/limitation (A) "approved
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Title: Synthesis of HTPB and CTPB Prepolymers by Anionic and Free-Radical
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Date of Document: Jan 1970. Technical Report: S-242.

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